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(54) Title: LIQUID INKS USING AN ORGANOSOL PREPARED FROM 3,3,5-TRIMETHYLCYCLOHEXYL METHACRYLATE

(57) Abstract: Gel organosols dispersions, and high solids color inks based upon these dispersions, featuring a carrier liquid having a Kauri-Butanol number less than 30 and a (co)polymeric steric stabilizer covalently bonded to a thermoplastic (co)polymeric core that is insoluble in the carrier liquid. The core includes units derived from 3,3,5-trimethylcyclohexyl methacrylate.

LIQUID INKS USING AN ORGANOSOL PREPARED FROM 3,3,5-TRIMETHYLCYCLOHEXYL METHACRYLATE

TECHNICAL FIELD

5   This invention relates to liquid ink compositions, in particular, to pigments dispersed in organosols to provide improved ink compositions and liquid toners for use in ink transfer, ionographic, electrographic and electrophotographic printing processes.

BACKGROUND

10   Liquid inks are widely used in a variety of printing processes, for example offset, intaglio, rotogravure, ink jet and electrographic printing. Many of the desired characteristics of the pigment dispersions used in the liquid inks are the same for each of the respective processes even though the final ink formulations may be substantially different. For example, the stability of the pigment dispersion both on

15   the shelf and under shear conditions is an important consideration regardless of the final use of the liquid ink. The art continuously searches for more stable pigment dispersions to provide more flexibility in ink formulations that in turn yields better efficiency and waste reduction in the various printing processes.

Electrographic printing refers to a printing process that uses an applied electric

20   field and charged particles to produce a printed image on a receptor material. The art generally refers to the charged particles as toners. Electrographic printing generally includes electrostatographic printing, ionographic printing, electrophotographic printing and the like. In electrophotographic applications, which include devices such as photocopiers, laser printers, facsimile machines and the like, the toners may be in

25   the form of dry particles or particles dispersed in a carrier liquid. Particles dispersed in a liquid medium for imaging purposes are generally referred to as liquid inks, liquid toners or liquid developers.

Generally, the electrophotographic process includes the steps of forming a latent electrostatic image on a charged photoconductor by exposing the

30   photoconductor to radiation in an imagewise pattern, developing the image by

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contacting the photoconductor with a liquid developer, and finally transferring the image to a receptor. The final transfer step may be performed either directly or indirectly through an intermediate transport member. The developed image is usually subjected to heat and/or pressure to permanently fuse the image to the receptor.

5   In the field of electrographic printing, particularly electrophotographic printing, a variety of both liquid and dry developing compositions have been employed to develop the latent electrostatic images. Dry toner compositions suffer from a number of disadvantages. For example, dry toners are known to be difficult to control during the latent image development and transfer processes; this leads to toner

10   scatter within the printer device and may create excessive amounts of dust and abrasive wear of the printer components. Some dry toner compositions must also be fixed by fusing at elevated temperature, which requires a large source of energy and may limit the choices of receptor materials to which the developed latent image may be transferred. Moreover, dry toners must be triboelectrically charged, which makes

15   the printing process very sensitive to both the temperature and humidity of the ambient air and may result in printing delays due to charge equilibration. The limited particle size of the toner is another disadvantage of dry toners. If the particle size is small, the dry toner can become airborne and create a potential health hazard due to inhalation of the particles. On the other hand, the larger particle sizes make it difficult

20   to obtain high resolution images.

Many of the disadvantages accompanying the use of dry toner compositions have been avoided by the use of liquid developers or toners. For example, liquid toners contain smaller particles than dry toners resulting in higher resolution images. In addition, liquid toners are not triboelectrically charged; therefore, they are much

25   less sensitive to changes in ambient temperature and humidity. Since the toner particles in a liquid developer are contained within a fluid phase, toner scatter and dust accumulation do not occur within the printer. In addition, the particles being contained within a liquid matrix will not become airborne thus eliminating the risk of inhalation of the particles.

30   Liquid toners typically comprise an electrically insulating liquid that serves as a carrier for a dispersion of charged particles known as toner particles composed of a colorant and a polymeric binder. A charge control agent is often included as a

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component of the liquid developer in order to regulate the polarity and magnitude of the charge on the toner particles. Liquid toners can be categorized into two primary classes, for convenience, the two classes will be referred to as conventional liquid toners and organosol toners.

5   Of particular utility are the class of liquid toners which make use of self-stable graft copolymers dispersed in an organic solvent (organosols) as polymeric binders to promote self-fixing of a developed latent image. U.S. Patent Nos. 3,753,760; 3,900,412; 3,991,226; 4,476,210; 4,789,616; 4,728,983; 4,925,766; 4,946,753; 4,978,598 and 4,988,602 describe compositions and uses of graft copolymer
10   organosols. Exemplary liquid electrophotographic, pigmented inks made using self-stable graft copolymer organosols are illustrated by Kosel in U.S. 3,900,412.

          Self-stable organosols are colloidal (0.1-1 micron diameter) particles of polymeric binder which are typically synthesized by nonaqueous dispersion polymerization in a low dielectric hydrocarbon solvent. These organosol particles are
15   sterically-stabilized with respect to aggregation by the use of a physically-adsorbed or chemically-grafted soluble polymer. Details of the mechanism of such steric stabilization are provided in Napper, D.H., Polymeric Stabilization of Colloidal Dispersions, Academic Press, New York, NY, 1983. Procedures for effecting the synthesis of self-stable organosols are known to those skilled in the art and are
20   described in Dispersion Polymerization in Organic Media, K.E. J. Barrett, ed., John Wiley: New York, NY, 1975.

          The most commonly used non-aqueous dispersion polymerization method is a free radical polymerization carried out when one or more ethylenically-unsaturated (typically acrylic) monomers, soluble in a hydrocarbon medium, are polymerized in
25   the presence of a preformed amphipathic polymer. The preformed amphipathic polymer, commonly referred to as the stabilizer, has two distinct ends, one essentially insoluble in the hydrocarbon medium, the other freely soluble. When the polymerization proceeds to a fractional conversion of monomer corresponding to a critical molecular weight, the solubility limit is exceeded and the polymer precipitates
30   from solution, forming a core particle. The amphipathic polymer then either adsorbs onto or covalently bonds to the core, which core continues to grow as a discrete particle. The particles continue to grow until monomer is depleted; the adsorbed

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amphipathic polymer "shell" acts to sterically-stabilize the growing core particles with respect to aggregation. The resulting core/shell polymer particles comprise a self-stable, nonaqueous colloidal dispersion (organosol) comprised of distinct spherical particles in the size (diameter) range 0.1-0.5 microns.

5   The resulting organosols can be subsequently converted to liquid toners by simple incorporation of the colorant (pigment) and charge director, followed by high shear homogenization, ball-milling, attritor milling, high energy bead (sand) milling or other means known in the art for effecting particle size reduction in a dispersion. The input of mechanical energy to the dispersion during milling acts to break down

10   aggregated pigment particles into primary particles (0.05-1.0 micron diameter) and to "shred" the organosol into fragments which adhere to the newly-created pigment surface, thereby acting to sterically-stabilize the pigment particles with respect to aggregation. The charge director may physically or chemically adsorb onto the pigment, the organosol or both. The result is a sterically-stabilized, charged,

15   nonaqueous pigment dispersion in the size range 0.1-2.0 microns, with typical toner particle diameters between 0.1-0.5 microns. Such a sterically-stabilized dispersion is ideally suited for use in high resolution printing.

       Rapid self-fixing is a critical requirement for liquid toner performance to avoid printing defects (such a smearing or trailing-edge tailing) and incomplete

20   transfer in high speed printing. A description of these types of defects and methods of preventing them using film forming compositions are described in U.S. Patent Nos. 5,302,482; 5,061,583; 4,925,766; 4,507,377; and 4,480,022.

       Another important consideration in formulating a liquid toner is the tack of the image on the final receptor. If the image has a residual tack, then the image may

25   become embossed or picked off when placed in contact with another surface. This is especially a problem when printed sheets are placed in a stack. If the image is tacky, it may transfer to the backside of the adjacent sheet. To address this concern, a film laminate or protective layer is typically placed over the surface of the image. This adds both extra cost of materials and extra process steps to apply the protective layer.

30   Another issue relating to images printed using liquid inks is image durability. Durability refers to the resistance of the printed images to damage by blocking when

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printed sheets are stacked, erasure resistance, scratch resistance and abrasion resistance. Generally, images printed with liquid toners are less durable than images printed using dry toners. The lower durability of liquid ink printed images may result from a variety of reasons known to those skilled in the art. These include the

5   relatively lower thickness of printed ink films made using liquid toners, the relatively lower adhesive strength of some liquid toners to their print receptors, and the relatively lower cohesive strength of some printed liquid toners due to the comparatively lower glass transition temperature of the polymeric binders used in these liquid inks.

10   Various methods have been proposed to improve the durability of printed images made using liquid toners. In particular, U.S. 5,886,067 describes improved durability liquid inks comprising a controlled crystallinity organosol that is not a gel organosol. The controlled crystallinity organosol comprises an insoluble core and a soluble graft stabilizer prepared from a side-chain or main chain crystallizing

15   polymeric moiety that independently and reversibly crystallizes at or above 22°C. Such controlled crystallinity organosols impart improved blocking resistance, erasure resistance, and abrasion resistance to liquid inks containing the organosol. Suitable crystallizing polymeric moieties for incorporation into a graft stabilizer include >C_{14} acrylic and methacrylic esters, which do not form gel organosols based upon

20   solubility parameter difference between graft stabilizer and carrier solvent.

SUMMARY OF THE INVENTION

In one aspect, the invention features a rapidly self-fixing ink useful as a liquid toner in ionographic or electrographic (electrophotographic or electrostatic) imaging and printing processes. The ink is comprised of a polymeric binder in the form of a

25   graft copolymer dispersed in an organic solvent or solvent blend having a Kauri-Butanol (KB) number less than 30, and optionally contains one or more colorants. The colorants may take the form of dyes or pigments. One or more charge controlling additives may optionally be added to the ink formulation.

"Kauri-Butanol" refers to an ASTM Test Method D1133-54T. The Kauri-

30   Butanol Number (KB) is a measure of the tolerance of a standard solution of kauri resin in 1-butanol to an added hydrocarbon diluent and is measured as the volume in

milliliters (mL) at 25°C of the solvent required to produce a certain defined degree of turbidity when added to 20 g of a standard kauri-1-butanol solution. Standard values are toluene (KB = 105) and 75% by volume of heptane with 25% by volume toluene (KB = 40). There is an approximately linear relationship between the Hildebrand

5   solubility parameter and the KB number for hydrocarbons: Hildebrand Solubility Parameter $(MPa^{1/2}) = 2.0455[6.3 + 0.03KB \text{ (mL)}]$.

The graft copolymer is comprised of a soluble or marginally insoluble high molecular weight (co)polymeric steric stabilizer ("graft stabilizer") covalently bonded to an insoluble, high molecular weight thermoplastic (co)polymeric backbone

10   ("organosol core") prepared from a monomer mixture that includes 3,3,5-trimethylcyclohexyl methacrylate (TCHMA). The homopolymer of TCHMA has a Tg substantially higher than ambient temperature (125°C), yet is soluble in many common carrier liquids. By incorporating TCHMA in the core, the core imbibes carrier liquid, thereby plasticizing and/or tackifying the core. As a result, the effective

15   Tg of an image prepared using a toner that includes the organosol is lowered while residual carrier liquid is present. This means that transfer efficiency will not be compromised as it would when preparing higher Tg organosol cores employing solely monomers whose homopolymers are insoluble in the carrier liquid. In addition, by using the higher Tg core formulations prepared with TCHMA, when the image is

20   adequately dried during the fusing process, the effective Tg of the organosol core can be close to or above ambient temperature (24°C). Consequently, the dried image is non-tacky and exhibits superior blocking resistance relative to formulations prepared using lower Tg cores.

The liquid inks will be described below with respect to electrophotographic

25   printing; however, it is to be understood that these liquid inks are not limited in their utility and may also be employed in other electrographic printing processes, high speed printing presses, photocopying apparatus, microfilm reproduction devices, facsimile printing, ink jet printer, instrument recording devices, and the like.

The details of one or more embodiments of the invention are set forth in the

30   accompanying drawings and the description below. Other features, objects, and advantages of the invention will be apparent from the description, and from the claims.

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DETAILED DESCRIPTION

A liquid ink composition is provided comprising a colorant and an organosol dispersed in a liquid or liquid blend having a Kauri-Butanol (KB) number less than 30. The organosol is an amphipathic copolymer comprised of a soluble or marginally insoluble high molecular weight (co)polymeric steric stabilizer covalently bonded to an insoluble, thermoplastic (co)polymeric core that includes units derived from TCHMA. The covalently bonded graft steric stabilizer preferably is crosslinked to such an extent that it behaves as an extremely high molecular weight copolymer near its incipient phase separation point in the dispersant liquid. The crosslinked graft stabilizer remains in a freely flowing, easily handled solution until the graft stabilizer is covalently bonded to the insoluble core, at which point an organosol is formed.

Superior stability of the dispersed toner particles with respect to aggregation is obtained when at least one of the polymers or copolymers (denoted as the stabilizer) is an amphipathic substance containing at least one oligomeric or polymeric component of molecular weight at least 500 that is solvated by the carrier liquid. In other words, the selected stabilizer, if present as an independent molecule, would have some finite solubility in the carrier liquid.

The solubility of a material in a given solvent may be predicted from the absolute difference in Hildebrand solubility parameter of the solute relative to the solvent. The solutes will exist as true solutions or in a highly solvated state when the absolute difference in Hildebrand solubility parameter is less than approximately 1.5 $MPa^{1/2}$. When the absolute difference in Hildebrand solubility parameter exceeds approximately 3.0 $MPa^{1/2}$, the solute will phase separate from the dispersant, forming a solid, insoluble, non-flowing, non-gelled mass. Those solutes having an absolute difference in Hildebrand solubility parameters between 1.5 $MPa^{1/2}$ and 3.0 $MPa^{1/2}$ are considered to be weakly solvated or marginally insoluble.

The solubility parameters of the graft stabilizers, as well as the carrier liquids in which the stabilizers are dispersed, are calculated using values for the Hildebrand solubility parameter of the monomers used to prepare the graft stabilizer and the carrier liquids obtained using the group contribution method developed by Small, P. A., J. Appl. Chem., 3, 71 (1953) using Small's group contribution values listed in Table 2.2 on page VII/525 in the Polymer Handbook, 3rd Ed., J. Brandrup & E. H.

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Immergut, Eds. John Wiley, NY, pp 519-557 (1989). The Hildebrand solubility

parameter for a copolymer may be calculated using a volume fraction weighting of

the individual Hildebrand solubility parameters for each monomer comprising the

copolymer. Similarly, the Hildebrand solubility parameter for a mixture may be

5   calculated using a volume fraction weighting of the individual Hildebrand solubility

parameters for each component of the mixture. Thus, the Hildebrand solubility

parameter for a mixture of solvents or polymerizable compounds may be calculated

using a volume fraction weighting of the individual Hildebrand solubility parameters

for each chemical compound comprising the solvent mixture.

10   Table 1 lists the Hildebrand solubility parameters for some common carrier

liquids used in an electrophotographic toner and the Hildebrand solubility parameters

and glass transition temperatures for some common monomers used in synthesizing

organosols.

Table I   Hildebrand Solubility Parameters

15   Solvent Values at 25°C

Solvent Name	Kauri-Butanol Number by ASTM Method D1133-54T (mL)	Hildebrand Solubility Parameter ($MPa^{1/2}$)
NORPAR 15 solvent	18	13.99
NORPAR 13 solvent	22	14.24
NORPAR 12 solvent	23	14.30
ISOPAR V solvent	25	14.42
EXXSOL D80 solvent	28	14.60

Source: Calculated from equation #31 of Polymer Handbook, 3rd Ed., J.

Brandrup E.H. Immergut, Eds. John Wiley, NY, p. VII/522 (1989).

Monomer Values at 25°C

Monomer Name	Hildebrand Solubility Parameter ($MPa^{1/2}$)	Glass Transition Temperature (°C)*
n-Octadecyl Methacrylate	16.77	-100
n-Octadecyl Acrylate	16.82	-55
Lauryl Methacrylate	16.84	-65
Lauryl Acrylate	16.95	-30
2-Ethylhexyl Methacrylate	16.97	-10
2-Ethylhexyl Acrylate	17.03	-55
n-Hexyl Methacrylate	17.13	-5
t-Butyl Methacrylate	17.16	107
n-Butyl Methacrylate	17.22	20
n-Hexyl Acrylate	17.30	-60
n-Butyl Acrylate	17.45	-55
Ethyl Methacrylate	17.90	66
Ethyl Acrylate	18.04	-24
Methyl Methacrylate	18.17	105
Vinyl Acetate	19.40	30
Methyl Acrylate	20.2	5

Calculated using Small's Group Contribution Method, Small, P.A. Journal of Applied Chemistry 3 p. 71 (1953). Using Group Contributions from Polymer Handbook, 3rd Ed., J. Brandrup E.H. Immergut, Eds., John Wiley, NY, p. VII/ 525 (1989).

* Polymer Handbook, 3rd Ed., J. Brandrup E.H. Immergut, Eds., John Wiley, NY, pp. VII/209-277 (1989).

The carrier liquid may be selected from a wide variety of materials that are known in the art, but preferably has a Kauri-Butanol number less than 30. The liquid is typically oleophilic, chemically stable under a variety of conditions, and electrically insulating. Electrically insulating refers to a liquid having a low dielectric constant

and a high electrical resistivity. Preferably, the liquid has a dielectric constant of less than 5, more preferably less than 3. Electrical resistivities of carrier liquids are typically greater than 10^9 Ohm-cm, more preferably greater than 10^{10} Ohm-cm. The carrier liquid preferably is also relatively nonviscous to allow movement of the

5   charged particles during development, and sufficiently volatile to permit its removal from the final imaged substrate, but sufficiently non-volatile to minimize evaporative losses in the developer. In addition, the carrier liquid should be chemically inert with respect to the materials or equipment used in the liquid electrophotographic process, particularly the photoreceptor and its release surface.

10   Examples of suitable carrier liquids include aliphatic hydrocarbons (n-pentane, hexane, heptane and the like), cycloaliphatic hydrocarbons (cyclopentane, cyclohexane and the like), aromatic hydrocarbons (benzene, toluene, xylene and the like), halogenated hydrocarbon solvents (chlorinated alkanes, fluorinated alkanes, chlorofluorocarbons, and the like), silicone oils and blends of these solvents.

15   Preferred carrier liquids include branched paraffinic solvent blends such as those commercially available under the trade designations ISOPAR G, ISOPAR H, ISOPAR K, ISOPAR L, ISOPAR M and ISOPAR V (available from Exxon Corporation, NJ), and most preferred carriers are the aliphatic hydrocarbon solvent blends such as those commercially available under the trade designations NORPAR

20   12, NORPAR 13 and NORPAR 15 (available from Exxon Corporation, NJ).

             The organosol is a graft copolymer prepared by chemically bonding a generally soluble (co)polymer to a generally insoluble (co)polymer resin core that includes units derived from TCHMA. Any number of reactions known to those skilled in the art may be used to effect grafting of the soluble polymeric stabilizer to

25   the organosol core during free radical polymerization. Common grafting methods include random grafting of polyfunctional free radicals; ring-opening polymerizations of cyclic ethers, esters, amides or acetals; epoxidations; reactions of hydroxyl or amino chain transfer agents with terminally-unsaturated end groups; esterification reactions (i.e., glycidyl methacrylate undergoes tertiary-amine catalyzed esterification

30   with methacrylic acid); and condensation polymerization.

             The composition of the graft stabilizer is normally selected such that the Hildebrand Solubility Parameter of the graft stabilizer (shell) closely matches that of

the carrier liquid in order to ensure that the stabilizer will be sufficiently solvated to dissolve in the carrier solvent. Virtually any polymerizable compound that exhibits a Hildebrand Solubility Parameter difference less than 3.0 MPa$^{1/2}$ relative to the carrier liquid may be used in forming a graft stabilizer. In addition, polymerizable

5   compounds that exhibit a Hildebrand Solubility Parameter difference greater than 3.0 MPa$^{1/2}$ relative to the carrier liquid may be used in forming a copolymeric graft stabilizer, provided that the effective Hildebrand Solubility Parameter difference for the stabilizer is less than 3.0 MPa$^{1/2}$ relative to the carrier liquid. The absolute difference in Hildebrand Solubility Parameter between the graft stabilizer (shell) and

10   the carrier liquid is preferably less than 2.6 MPa$^{1/2}$.

Preferred polymerizable compounds useful in forming the graft stabilizer are the C_6-C_{30} acrylic and methacrylic esters. Examples of suitable polymerizable compounds for use in the graft stabilizer composition non-exclusively include monomers such as, hexyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, dodecyl

15   (lauryl) acrylate, octadecyl (stearyl) acrylate, behenyl acrylate, hexyl methacrylate, 2-ethylhexyl(methacrylate), decyl acrylate, dodecyl (lauryl) methacrylate, octadecyl (stearyl) methacrylate and other alkyl acrylates and methacrylates.

Preferrably, the polymerizable compounds are also crystallizable compounds having crystallization (melting) temperatures above room temperature (25°C). Such

20   crystallizable, polymerizable compounds are particularly useful in forming graft stabilizers that yield organosols and inks exhibiting improved image durability, including blocking and erasure resistance. Crystallizable, polymerizable compounds suitable for incorporation into a graft stabilizer include >C_{14} acrylic and methacrylic esters. Preferable crystallizable, polymerizable compounds include octadecyl acrylate

25   and behenyl acrylate.

Other monomers, macromers, or polymers may be used either alone or in conjunction with the aforementioned materials, including melamine and melamine formaldehyde resins, phenol formaldehyde resins, epoxy resins, polyester resins, styrene and styrene/acrylic copolymers, acrylic and methacrylic esters, cellulose

30   acetate and cellulose acetate-butyrate copolymers, and poly(vinyl butyral) copolymers.

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Preferred molecular weight ranges for the graft stabilizer are 5,000-1,000,000
Daltons (Da), more preferably = 50,000-500,000 Da, most preferably = 150,000-
250,000 Da. The polydispersity of the graft stabilizer also has an affect on imaging
and transfer performance of the liquid toners. Generally, it is desirable to maintain the
5   polydispersity (the ratio of the weight-average molecular weight to the number
average molecular weight) of the graft stabilizer below 15, more preferably below 5,
most preferably below 2.5.

As discussed above, the organosol is a graft copolymer dispersion formed by
covalently bonding the graft stabilizer to an insoluble resin core. The grafting
10   reaction generally occurs between a grafting site incorporated into the graft stabilizer
and a reaction site in the polymerizing or polymerized core. Preferably, the grafting .
reaction proceeds by reaction of an isocyanate to a hydroxyl group to form a urethane
linkage between the stabilizer and the core. The grafting site is preferably formed by
incorporating hydroxyl groups into the graft stabilizer during a first free radical
15   polymerization and catalytically reacting all or a portion of these hydroxyl groups
with an ethylenically unsaturated aliphatic isocyanate (e.g. meta-
isopropenyldimethylbenzyl isocyanate [TMI] or isocyanatoethylmethacrylate [IEM])
to form a urethane linkage during a subsequent non-free radical reaction step. The
graft stabilizer is then covalently bonded to the nascent insoluble acrylic (co)polymer
20   core via reaction of the unsaturated vinyl group of the grafting site with ethylenically-
unsaturated core monomers (e.g. vinyl esters, particularly acrylic and methacrylic
esters with carbon numbers < 6 or vinyl acetate; vinyl aromatics, such as styrene;
acrylonitrile; n-vinyl pyrrolidone; vinyl chloride and vinylidene chloride) during a
subsequent free radical polymerization step.

25   Other methods of effecting grafting of the preformed polymeric stabilizer to
the incipient insoluble core particle are known to those skilled in the art. For
example, alternative grafting protocols are described in sections 3.7-3.8 of Barrett
Dispersion Polymerization in Organic Media, K. E. J. Barrett, ed., (John Wiley: New
York, 1975), pp. 79-106. A particularly useful method for grafting the polymeric
30   stabilizer to core utilizes an anchoring group. The function of the anchoring groups is
to provide a covalent link between the core part of the particle and the soluble
component of the steric stabilizer. Suitable monomers containing anchoring groups

include: adducts of alkenylazlactone comonomers with an unsaturated nucleophile containing hydroxy, amino, or mercaptan groups, such as 2-hydroxyethylmethacrylate, 3-hydroxypropylmethacrylate, 2-hydroxyethylacrylate, pentaerythritol triacrylate, 4-hydroxybutyvinylether, 9-octadecen-1-ol, cinnamyl

5   alcohol, allyl mercaptan, methallylamine; and azlactones, such as 2-alkenyl-4,4-dialkylazlactone of the structure
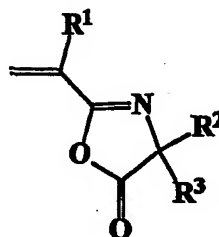
where R^1 = H, or alkyl having 1 to 5 carbons, preferably one carbon, R^2 and R^3 are independently lower alkyl groups having 1 to 8 carbons, preferably 1 to 4 carbons.

10   Most preferably, however, the grafting mechanism is accomplished by grafting an ethylenically-unsaturated isocyanate (e.g., dimethyl-m-isopropenyl benzylisocyanate, available from American Cyanamid) to hydroxyl groups previously incorporated into the graft stabilizer precursor (i.e., hydroxy ethyl methacrylate).

The insoluble organosol core is the dispersed phase of the graft copolymer

15   dispersion. The core polymer is generally made *in situ* by copolymerization with the stabilizer monomer. The solubility parameter of the core is generally chosen such that it differs substantially from that of the dispersion medium in order to ensure that the core monomers will phase separate during dispersion polymerization (forming the core). Preferably, the Hildebrand solubility parameter difference between the core as

20   a whole and the carrier liquid exceeds 3.0 $MPa^{1/2}$.

The core is prepared from a monomer mixture that includes TCHMA. The homopolymer of TCHMA itself is very soluble in the dispersant medium. However, it can be incorporated into the core in small amounts with monomers which, when polymerized, are not very soluble in the carrier liquid; examples of the latter include

25   C_1-C_5 acrylate and methacrylate esters such as, methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate), butyl methacrylate, styrene and

vinyl acetate. The effect of incorporating TCHMA into the organosol core will generally be to cause carrier liquid absorption or swelling of the core. This can be particularly useful when higher core T_g's are desired, for example, to improve image durability, but when rapid self-fixing of the ink is still required in the imaging

5   process. By increasing the affinity of the core for the carrier liquid, the carrier liquid will be imbibed into the core and may act to plasticize the core, permitting rapid self-fixing of an ink comprising a high core T_g organosol even at temperatures below the normal minimum film-forming temperature.

Preferably, the Hildebrand solubility parameter difference between the core as

10   a whole and the carrier liquid exceeds 3.0 $MPa^{1/2}$. The amount of TCHMA incorporated into the core typically ranges between 1-30% w/w, more preferably 5-20% w/w.

Other polymers which may be used either alone or in conjunction with the aforementioned materials, include melamine and melamine formaldehyde resins,

15   phenol formaldehyde resins, epoxy resins, polyester resins, styrene and styrene/acrylic copolymers, acrylic and methacrylic esters, cellulose acetate and cellulose acetate-butyrate copolymers, and poly(vinyl butyral) copolymers.

If the core/shell ratio is too high, there may be insufficient graft stabilizer present to sterically-stabilize the organosol with respect to aggregation. If the

20   core/shell ratio is too low, the polymerization may have insufficient driving force to form a distinct particulate phase resulting in a copolymer solution, not a self-stable organosol dispersion. The optimal weight ratio of the resin core to the stabilizer shell is on the order of 1/1 to 15/1, preferably between 2/1 and 10/1, and most preferably between 4/1 and 8/1.

25   The particle size of the organosol also influences the imaging, drying, and transfer characteristics of the liquid inks. Preferably, the primary particle size (determined with dynamic light scattering) of the organosol is between about 0.05 and 5.0 microns, more preferably between 0.15 and 1 micron, most preferably between 0.20 and 0.50 microns.

30   A liquid ink utilizing the aforementioned organosol comprises colorant particles embedded in the thermoplastic organosol resin. Useful colorants are well

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known in the art and include materials such as dyes, stains, and pigments. Preferred colorants are pigments that may be incorporated into the polymer resin, are nominally insoluble in and nonreactive with the carrier liquid, and are useful and effective in making visible the latent electrostatic image. Examples of suitable colorants include:

5   phthalocyanine blue (C.I. Pigment Blue 15:1, 15:2, 15:3, 15:4 and 16), monoarylide yellow (C.I. Pigment Yellow 1, 3, 65, 73 and 74), diarylide yellow (C.I. Pigment Yellow 12, 13, 14, 17 and 83), arylamide (Hansa) yellow (C.I. Pigment Yellow 10, 97, 105 and 111), Pigment Yellow 138, azo red (C.I. Pigment Red 3, 17, 22, 23, 38, 48:1, 48:2, 52:1, 81, 81:1, 81:2, 81:3 and 179), quinacridone magenta (C.I. Pigment

10   Red 122, 202 and 209) and black pigments such as finely divided carbon (CABOT MONARCH 120, CABOT REGAL 300R, CABOT REGAL 350R, VULCAN X72) and the like.

For some applications, it is desirable to use the organosol without an added colorant (dye or pigment) to provide a clear protective overcoat for an underlying

15   image on a permanent receptor. In such cases, the transparent ink may be applied, for example, using well-known coating or electrographic development processes, onto either a temporary imaging receptor or permanent imaging receptor. In the event that the transparent organosol is applied to a permanent image receptor, the organosol should be coated onto the surface of the receptor and any underlying image in order to

20   perform as a protective overcoat. In the event that the organosol is applied to a temporary image receptor, consideration must be given to the reversal of layers that occurs during offset transfer processes. Thus, it may be necessary to coat or develop the transparent organosol as the first layer on a photoreceptive element upon which a multi-colored image is constructed in order to insure that the transparent organosol

25   acts as a protective topcoat upon offset transfer of the image to a permanent image receptor.

The optimal weight ratio of resin (organosol) to colorant in the toner particles is on the order of 1/1 to 20/1, preferably between 3/1 and 10/1, and most preferably between 5/1 and 8/1. The total dispersed material in the carrier liquid typically

30   represents 0.5 to 70 weight percent, preferably between 1 and 25 weight percent, most preferably between 2 and 17 weight percent of the total liquid developer composition.

The organosols can be used to fabricate liquid electrophotographic toners that exhibit excellent imaging characteristics in liquid immersion development. For example, the organosol liquid toners exhibit low bulk conductivity, low free phase conductivity, and low charge/mass and high mobility, all of which are desirable

5   characteristics for producing high resolution, background-free images with high optical density. In particular, the low bulk conductivity, low free phase conductivity, and low charge/mass of the toners allow them to achieve high developed optical density over a wide range of solids concentrations, thus improving their extended printing performance relative to conventional toners. In addition, color liquid toners

10   based upon these organosols on development form transparent films that transmit incident light, consequently allowing the photoconductor layer to discharge.

An electrophotographic liquid toner may be formulated by incorporating a charge control agent into the liquid ink. The charge control agent, also known as a charge director, provides uniform charge polarity of the toner particles. The charge

15   director may be incorporated into the toner particles using a variety of methods such as chemically reacting the charge director with the toner particle, chemically or physically adsorbing the charge director onto the toner particle (resin or pigment), or chelating the charge director to a functional group incorporated into the toner particle. A preferred method is via a functional group built into the graft stabilizer. The charge

20   director imparts an electrical charge of selected polarity onto the toner particles. Any number of charge directors described in the art may be used. For example, the charge director may be introduced in the form of metal salts consisting of polyvalent metal ions and organic anions as the counterion. Suitable metal ions include Ba(II), Ca(II), Mn(II), Zn(II), Zr(IV), Cu(II), Al(III), Cr(III), Fe(II), Fe(III), Sb(III), Bi(III), Co(II),

25   La(III), Pb(II), Mg(II), Mo(III), Ni(II), Ag(I), Sr(II), Sn(IV), V(V), Y(III), and Ti(IV). Suitable organic anions include carboxylates or sulfonates derived from aliphatic or aromatic carboxylic or sulfonic acids, preferably aliphatic fatty acids such as stearic acid, behenic acid, neodecanoic acid, diisopropylsalicylic acid, octanoic acid, abietic acid, naphthenic acid, octanoic acid, lauric acid, tallic acid, and the like. Preferred

30   positive charge directors are the metallic carboxylates (soaps) described in U.S. Patent 3,411,936, incorporated herein by reference, which include alkaline earth- and heavy-metallic salts of fatty acids containing at least 6-7 carbons and cyclic aliphatic acids

including naphthenic acid; more preferred are polyvalent metal soaps of zirconium and aluminum; most preferred is the zirconium soap of octanoic acid (Zirconium HEX-CEM from Mooney Chemicals, Cleveland, OH).

The preferred charge direction levels for a given toner formulation will depend upon a number of factors, including the composition of the graft stabilizer and organosol, the molecular weight of the organosol, the particle size of the organosol, the core/shell ratio of the organosol, the pigment used in making the toner, and the ratio of organosol to pigment. In addition, preferred charge direction levels will also depend upon the nature of the electrophotographic imaging process, particularly the design of the developing hardware and photoreceptive element. Those skilled in the art, however, know how to adjust the level of charge direction based on the listed parameters to achieve the desired results for their particular application.

The conductivity of a liquid toner has been well established in the art as a measure of the effectiveness of a toner in developing electrophotographic images. A range of values from $1.0x10^{-11}$ mho/cm to $10.0x10^{-11}$ mho/cm has been disclosed as advantageous in U.S. 3,890,240. High conductivities generally indicate inefficient association of the charges on the toner particles and are seen in the low relationship between current density and toner deposited during development. Low conductivities indicate little or no charging of the toner particles and lead to very low development rates. The use of charge director compounds to ensure sufficient charge associated with each particle is a common practice. There has, in recent times, been a realization that even with the use of charge directors there can be much unwanted charge situated on charged species in solution in the carrier liquid. Such charge produces inefficiency, instability and inconsistency in the development. U.S. Patent No. 4,925,766 discloses that at least 40%, and preferably at least 80%, of the total charge in the liquid toner should be situated and remain on the toner particles.

Suitable efforts to localize the charges onto the toner particles and to ensure that there is substantially no migration of charge from those particles into the liquid, and that no other unwanted charge moieties are present in the liquid, give substantial improvements. A measure of the required properties is the ratio between the conductivity of the carrier liquid as it appears in the liquid toner and the conductivity of

the liquid toner as a whole. This ratio is preferably less than 0.6, more preferably less than 0.4, and most preferably less than 0.3.

Any number of methods may be used for effecting particle size reduction of the pigment in preparation of the liquid toners. Some suitable methods include high shear homogenization, ball-milling, attritor milling, high energy bead (sand) milling, basket milling or other means known in the art. Preferably, the ink is milled in an attritor, vertical bead mill, or basket mill to avoid overshearing the organosol, which can cause an undesirable reduction in ink stability and adversely affect charge characteristics such as ink conductivity.

In electrophotographic and electrographic processes, an electrostatic image is formed on the surface of a photoreceptive element or dielectric element. The photoreceptive element or dielectric element may be an intermediate transfer drum or belt, or the substrate for the final toned image itself, as described by Schmidt, S. P. and Larson, J. R. in Handbook of Imaging Materials Diamond, A. S., Ed: Marcel Dekker: New York; Chapter 6, pp 227-252, and U. S. Patent Nos. 4,728,983, 4,321,404, and 4,268,598.

In electrography, a latent image is typically formed by (1) placing a charge image onto the dielectric element (typically the receiving substrate) in selected areas of the element with an electrostatic writing stylus or its equivalent to form a charge image, (2) applying toner to the charge image, and (3) fixing the toned image. An example of this type of process is described in U.S. Patent No. 5,262,259.

Images formed by the present invention may be of a single color or a plurality of colors. Multicolor images can be prepared by repetition of the charging and toner application steps. Examples of electrophotographic methods suitable for producing full color reproductions are described by U.S. Patent Nos. 2,297,691; 2,752,833; 2,986,466; 3,690,756; 4,403,848; 4,370,047; 4,467,334; 4,728,983; U.S. 5,650,253; U.S. 5,916,718; and European Patent Application No. 0,453,256. Examples of suitable transfer and fixing processes are described in U.S. Patent Nos. 4,337,303 and 5,108,865.

In electrophotography, the electrostatic image is typically formed on a drum or belt coated with a photoreceptive element by (1) uniformly charging the

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photoreceptive element with an applied voltage, (2) exposing and discharging portions of the photoreceptive element with a radiation source to form a latent image, (3) applying a toner to the latent image to form a toned image, and (4) transferring the toned image through one or more steps to a final receptor sheet. In some applications,

5   it is sometimes desirable to fix the toned image using a heated pressure roller or other fixing methods known in the art.

While the electrostatic charge of either the toner particles or photoreceptive element may be either positive or negative, electrophotography is preferably carried out by dissipating charge on a positively charged photoreceptive element. Toner is

10   then applied to the regions in which the positive charge was dissipated using a liquid toner immersion development technique. This development may be accomplished by using a uniform electric field produced by a development electrode spaced near the photoreceptive element surface. A bias voltage is applied to the electrode intermediate to the initially charged surface voltage and the exposed surface voltage

15   level. The voltage is adjusted to obtain the required maximum density level and tone reproduction scale for halftone dots without any background deposited. Liquid toner is then caused to flow between the electrode and the photoreceptive element. The charged toner particles are mobile in the field and are attracted to the discharged areas on the photoreceptive element while being repelled from the undischarged non-image

20   areas. Excess liquid toner remaining on the photoreceptive element is removed by techniques well known in the art. Thereafter, the photoreceptive element surface may be force dried or allowed to dry at the ambient conditions.

Particularly useful electrophotographic processes for forming a multi-colored image on a receptor are described in U.S. 5,061,583, U.S. 5,650,253 and U.S.

25   5,916,718, which are incorporated herein by reference. The process disclosed in U.S. 5,650,253 basically involves the steps of (i) applying a uniform positive charge of approximately 700 volts on the surface of a photoreceptive element, (ii) exposing and partially discharging the surface of the photoreceptive element with a laser scanning device in an image-wise pattern to create a latent image, (iii) applying a liquid color

30   toner to the latent image to form both a toned image and a uniform surface charge on the photoreceptive element, (iv) removing excess liquid toner, (v) drying the toned image, and (vi) transferring the toned image either directly or indirectly onto a final

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receptor. To form multi-colored images, steps (i) through (iv) are repeated until all the desired colors are formed on the photoreceptive element prior to transferring the images either directly or indirectly onto a final receptor.

The process disclosed in U.S. 5,916,718 is similar to that of U.S. U.S.

5   5,650,253, except that processes (ii) through (v) are repeated in forming a multi-colored image. Unlike conventional electrophotographic processes, this process of forming multi-colored images may be accomplished without erasing the residual charge and recharging the surface of the photoreceptive element prior to scanning and developing a subsequent image. The liquid toner of the present invention provides

10   sufficient charge in the imaged areas to allow the creation of a subsequent latent image without erasing and recharging the surface. Alternatively, the process of U.S. 5,916,718 may be carried out in a manner such that steps (ii)-(vi) are repeated in forming a multi-colored image, in which case the multi-colored image may be built up on an intermediate transfer element, or may be built up on the final image receptor.

15   These methods make use of an offset transfer process incorporating as an element an intermediate transfer roller which is coated with a silicone or fluorosilicone elastomer composition, which is heated to between 80-100°C, and which applies a force of approximately 40-80 lb_f across the entire contact zone with the photoreceptor. One suitable coating composition for the transfer roller is the Dow

20   Corning 94-003 fluorosilicone elastomer heated to between 85-95°C. Preferred elastomeric coating compositions are disclosed in U.S. 5,965,314, which is incorporated herein by reference.

The substrate for receiving the image from either the photoreceptive element in electrophotographic printing or the dielectric element in electrostatic printing can

25   be any commonly used receptor material, such as paper, coated paper, polymeric films and primed or coated polymeric films, particularly adhesive coated polymeric films. Suitable polymeric films include polyesters, plasticized and compounded polyvinyl chloride (PVC), acrylics, polyurethanes, polyethylene/acrylic acid copolymers, SURLYN and polyvinyl butyrals. Commercially available composite

30   materials such as those having the trade designations SCOTCHCAL, SCOTCHLITE, and PANAFLEX are also suitable for preparing substrates.

The transfer of the formed image from the surface of photoreceptor or dielectric element to the final receptor or transfer medium may be enhanced by the incorporation of a release-promoting material within the dispersed particles used to form the image. The incorporation of a silicone-containing material or a fluorine-

5   containing material in the outer (shell) layer of the particle facilitates the efficient transfer of the image.

In multicolor electrographic imaging, the toners may be applied to the surface of the dielectric element or photoreceptive element in any order, but for colorimetric reasons, bearing in mind the inversion that occurs on transfer, it is sometimes

10   preferred to apply the images in a specified order depending upon the transparency and intensity of the colors. A preferred order for direct imaging or double transfer process is yellow, magenta, cyan and black; for a single transfer process, the preferred order is black, cyan, magenta, and yellow. Yellow is generally imaged first to avoid contamination from other toners and black is generally imaged last due to the black

15   toner acting as a filter of the radiation source.

Overcoating of the transferred image may optionally be carried out to protect the image from physical damage and/or actinic damage. Compositions for overcoatings are well-known in the art and typically comprise a clear film-forming polymer dissolved or suspended in a volatile solvent. An ultraviolet light absorbing

20   agent may optionally be added to the coating composition. Lamination of protective layers to the image-bearing surface is also well known in the art and may be used.

In order to function most effectively, liquid toners preferably have conductance values in the range of 50 to 1200 picomho-cm^{-1} at their working concentrations. Liquid toners prepared according to the present invention preferably

25   have conductance values of from 50 to 500 picomho-cm^{-1} for a dispersion containing 3% by weight solids. Toners are usually prepared in a concentrated form to conserve storage space and reduce transportation costs. In order to use the toners in the printer, the concentrate is diluted with additional carrier liquid to give what is termed the working strength liquid toner.

30   These and other aspects of the present invention are demonstrated in the illustrative examples that follow.

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EXAMPLES

Glossary of Chemical Abbreviations & Chemical Sources

The following raw materials were used to prepare the polymers in the examples which follow:

5   The catalysts used in the examples are Azobisisobutyronitrile (designated as AIBN under the trade designation VAZO-64 available from DuPont Chemicals, Wilmington, DE); and Dibutyl Tin Dilaurate (designated as DBTDL, commercially available from Aldrich Chemical Co., Milwaukee, WI). The monomers are all commercially available from Scientific Polymer Products, Inc., Ontario, NY unless
10   designated otherwise.

The monomers used in the examples are designated by the following abbreviations: Dimethyl-m-isopropenyl benzylisocyanate (TMI, available from CYTEC Industries, West Paterson, NJ); Ethyl Acrylate (EA); 2-Ethylhexyl Methacrylate (EHMA); 2-Hydroxyethyl Methacrylate (HEMA); and 3,3,5-
15   trimethylcyclohexyl methacrylate (TCHMA).

Analytical Test Methods

The following test methods were used to characterize the polymers and inks in the examples that follow:

Percent Solids of Graft Stabilizer, Organosol, and Liquid Toner

20   Percent solids of the graft stabilizer solutions, and the organosol and ink dispersions, were determined gravimetrically using a halogen lamp drying oven attachment to a precision analytical balance (Mettler Instruments Inc., Hightstown, NJ). Approximately two grams of sample were used in each determination of percent solids using this sample drydown method.

25 ### Graft Stabilizer Molecular Weight

Various properties of the graft stabilizer have been determined to be important to the performance of the stabilizer, including molecular weight and molecular weight

polydispersity. Graft stabilizer molecular weight is normally expressed in terms of the weight average molecular weight (M_w), while molecular weight polydispersity is given by the ratio of the weight average molecular weight to the number average molecular weight (M_w/M_n). Molecular weight parameters were determined for graft

5   stabilizers with gel permeation chromatography (GPC) using tetrahydrofuran as the carrier solvent. Absolute M_w was determined using a Dawn DSP-F light scattering detector (Wyatt Technology Corp, Santa Barbara,CA), while polydispersity was evaluated by ratioing the measured M_w to a value of M_n determined with an Optilab 903 differential refractometer detector (Wyatt Technology Corp, Santa Barbara, CA).

10   Organosol Particle Size

Organosol particle size was determined by dynamic light scattering on a diluted toner sample (typically < 0.0001 g/ml) using a Malvern Zetasizer III Photon Correlation Spectrometer (Malvern Instruments Inc, Southborough, MA). The dilute samples were ultrasonicated for one minute at 100 watts and 20 kiloHz (kHz) prior to

15   measurement. Dynamic light scattering provides a fast method of determining the particle translational diffusion coefficent, which can be related to the z-average particle diameter without detailed knowledge of the optical and physical properties (i.e. refractive index, density and viscosity) of the organosol. Details of the method are described in Chu (Chu, B., Laser Scattering Academic Press, NY 1974, 11A).

20   Since the organosols are comprised of nearly monodisperse, uniform spherical particles, dynamic light scattering provides an absolute measure of particle size for particles having diameters between 25-2500 nm.

Liquid Toner Properties

The characterization of a liquid toner requires the measurement of a number of

25   physical and chemical properties of the toner, as well as direct evaluation of image quality obtained by developing the toner in a LEP imaging mechanism. The measured toner characteristics can be roughly broken down into size-related properties (particle size), charge-related properties (bulk and free phase conductivity, dynamic mobility and zeta potential, and charge/developed reflectance optical density

30   (Q/ROD), a parameter which is directly proportional to the toner charge/mass.

Particle Size

Toner particle size distributions were determined using a Horiba LA-900 laser diffraction particle size analyzer (Horiba Instruments, Inc, Irvine, CA). Toner samples were diluted approximately 1/500 by volume and sonicated for one minute at
5   150 watts and 20 kHz prior to measurement. Toner particle size was expressed on a number-average basis in order to provide an indication of the fundamental (primary) particle size of the ink particles.

Toner Conductivity

The liquid toner conductivity (bulk conductivity, k_b) was determined at
10   approximately 18 Hz using a Scientifica model 627 conductivity meter (Scientifica Instruments, Inc., Princeton, NJ). In addition, the free (dispersant) phase conductivity (k_f) in the absence of toner particles was also determined. Toner particles were removed from the liquid milieu by centrifugation at 5°C for 1-2 hours at 6,000 rpm (6,110 relative centrifugal force) in a Jouan MR1822 centrifuge (Winchester, VA).
15   The supernatant liquid was then carefully decanted, and the conductivity of this liquid was measured using a Scientifica Model 627 conductance meter. The percentage of free phase conductivity relative to the bulk toner conductivity was then determined as: 100% (k_f/k_b).

Particle Mobility

20   Toner particle electrophoretic mobility (dynamic mobility) was measured using a Matec MBS-8000 Electrokinetic Sonic Amplitude Analyzer (Matec Applied Sciences, Inc., Hopkinton, MA). Unlike electrokinetic measurements based upon microelectrophoresis, the MBS-8000 instrument has the advantage of requiring no dilution of the toner sample in order to obtain the mobility value. Thus, it was
25   possible to measure toner particle dynamic mobility at solids concentrations actually preferred in printing. The MBS-8000 measures the response of charged particles to high frequency (1.2 MHz) alternating (AC) electric fields. In a high frequency AC electric field, the relative motion between charged toner particles and the surrounding dispersion medium (including counter-ions) generates an ultrasonic wave at the same
30   frequency of the applied electric field. The amplitude of this ultrasonic wave at 1.2 MHz can be measured using a piezoelectric quartz transducer; this electrokinetic

sonic amplitude (ESA) is directly proportional to the low field AC electrophoretic mobility of the particles. The particle zeta potential can then be computed by the instrument from the measured dynamic mobility and the known toner particle size, dispersant liquid viscosity, and liquid dielectric constant.

5   Particle Charge

Toner charge/mass is an important, albeit difficult to determine parameter useful in predicting the development characteristics (e.g. optical density, overtoning uniformity) for liquid toners. The difficult in determining charge/mass for liquid toners arises from the low developed toner mass (typically 50-200 micro grams/cm^2)

10 associated with the desired developed optical densities (typically > 1.2 reflectance optical density units). A related parameter which is directly proportional to toner charge/mass is the toner charge/developed optical density. This parameter was determined by plating ink particles in distinct bands covering a range of known plating potentials onto a dielectric sheet coated with a silicone release layer while

15 simultaneously monitoring the total current flow with a sensitive electrometer. The resulting plated toner layer was then air dried and transferred using an offset transfer process to plain paper. The reflectance optical density of the completely transferred toner film on paper was determined using a Greteg SPM50 reflectance optical densitometer (Greteg Instruments Inc., Regensdorf, Sitzerland). The ratio of the total

20 current to the product of the plated toner area and the developed optical density yields the charge/ROD value for that toner, i.e. Charge/ROD = (Total Current)/[(Plated Area)(Reflectance Optical Density)].

Graft Stabilizers

In the following example of graft stabilizer preparation, it will be convenient

25 to summarize the compositional details of each particular graft stabilizer or graft stabilizer precursor by ratioing the weight percentage of monomers employed in the synthesis. For example, a graft stabilizer designated EHMA/HEMA-TMI (97//3-4.7 %w/w) is made from a graft stabilizer precursor which is a copolymer consisting of 97% weight percent EHMA and 3% weight percent HEMA, to which is covalently

30 bonded a grafting site consisting of 4.7 weight percent TMI based on the total weight of the graft stabilizer precursor.

Example 1

A 5000 ml 3-necked round bottom flask equipped with a condenser, a thermocouple connected to a digital temperature controller, a nitrogen inlet tube connected to a source of dry nitrogen, and an overhead mechanical agitator, was

5 charged with a mixture of 2561 g of NORPAR 12 solvent, 849 g of EHMA, 26.8 g of 96% HEMA, and 8.31 g of AIBN. While mechanically stirring the mixture, the reaction flask was purged with dry nitrogen for 30 minutes at a flow rate of approximately 2 liters/min. A hollow glass stopper was then inserted into the open end of the condenser and the nitrogen flow rate was reduced to approximately 0.5

10 liters/min. The mixture was heated to 70°C for 16 hours, at which time the conversion was quantitative.

The mixture was heated to 90°C and held at that temperature for 1 hour to destroy any residual AIBN, then was cooled back to 70°C. The nitrogen inlet tube was then removed, and 13.6 g of DBTDL were added to the mixture, followed by

15 41.1 g of TMI. The TMI was added drop wise over the course of approximately five minutes while magnetically stirring the reaction mixture. The nitrogen inlet tube was replaced, the hollow glass stopper in the condenser was removed, and the reaction flask was purged with dry nitrogen for 30 minutes at a flow rate of approximately 2 liters/min. The hollow glass stopper was reinserted into the open end of the

20 condenser and the nitrogen flow rate was reduced to approximately 0.5 liters/min. The mixture was allowed to react at 70°C for 6 hours, at which time the conversion was quantitative.

The mixture was then cooled to room temperature. The percent solids of the liquid mixture was determined as 26.0% using the infrared drying method describe

25 above. Subsequent determination of molecular weight was made using the GPC method described above. The copolymer has a M_w of 199,000 Da and M_w/M_n of 2.93. The product is a copolymer of EHMA and HEMA having random side chains of TMI and is designated as EHMA/HEMA-TMI (97/3-4.7% w/w).

Organosol Examples

30 In the following examples of organosol preparation, it will be convenient to summarize the composition of the organosol in terms of the ratio of the total weight of

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monomers comprising the organosol core relative to the total weight of monomers comprising the organosol shell. The ratio is referred to as the core/shell ratio of the organosol. In addition, it will be useful to summarize the compositional details of each particular organosol by ratioing the weight percentages of monomers used to

5   create the shell and the core. For example, an organosol designated EHMA/HEMA-TMI//MMA/EA (97/3-4.7//25/75 % w/w) is made form shell comprised of graft stabilizer precursor which is a copolymer consisting of 97 weight percent of EHMA and 3 weight percent of HEMA, to which is covalently bonded a grafting site consisting of 4.7 weight percent of TMI based on the total weight of graft stabilizer

10   precursor. The graft stabilizer is covalently bonded to a core that is comprised of 25 weight percent MMA and 75 weight percent of EA.

Example 2

This example illustrates the use of the graft stabilizer in Example 1 to prepare an organosol with a core/shell ratio of 8/1. A 5000 mL 3-necked round bottom flask

15   equipped with an overhead mechanical stirrer, condenser, a thermocouple connected to a digital temperature controller, and a nitrogen inlet tube connected to a source of dry nitrogen was charged with a mixture of 2943 g of NORPAR 12 solvent, 179.5 g of the graft stabilizer from Example 1 at 26.0% solids, 113.1 g of TCHMA, 65.3 g of MMA, 196 g of EA, and 6.3 g of AIBN. While mechanically stirring, the reaction

20   flask was purged with dry nitrogen for 30 minutes at a flow rate of approximately 2 liters/minute. The nitrogen flow rate was then adjusted to approximately 0.5 liters/min. The mixture was heated to 70°C with stirring, and allowed to polymerize at 70°C for 16 hours, at which time the organosol was cooled to room temperature.

Approximately 350 g of n-heptane were added to the cooled organosol and the

25   resulting mixture was stripped of residual monomer using a rotary evaporator equipped with a dry ice/acetone condenser and operating at a temperature of 95°C, and reducing the vacuum gradually so as to maintain an adequate condensate collection rate to approximately 15 mm Hg. The stripped organosol was cooled to room temperature, yielding an opaque white dispersion.

This organosol is designated EHMA/HEMA-TMI//TCHMA/MMA/EA (97/3-4.7//30/18/52 % w/w) having a calculated core T_g equal to 24^0C. DSC (differential scanning calorimetry) showed the measured Tg to be 17.2°C. The percent solids of this organosol was determined as 16.75% using the halogen drying method outlined

5   above. Subsequent determination of average particle size was made using the dynamic light scattering method described above. The organosol had a z-average diameter of 122 nm.

Comparative Example A

The procedure of Example 2 was followed except that the organosol was

10   prepared by reacting the graft stabilizer with 93.3 g MMA, 280 g EA, and 6.3 g AIBN. The resulting organosol is designated EHMA/HEMA-TMI///MMA/EA (97/3-4.7//25/75 % w/w) having a calculated core T_g equal to -1^0C. DSC (differential scanning calorimetry) showed the measured Tg to be 5.7°C. The percent solids of this organosol was determined as 16.0% using the halogen drying method outlined above.

15   Subsequent determination of average particle size was made using the dynamic light scattering method described above. The organosol had a z-average diameter of 220 nm.

Liquid Toner Examples

Example 3

20   This is an example of preparing a black liquid toner at an organosol/pigment ratio of 6 using the organosol prepared in Example 2 at core/shell ratio of 8. The organosol of Example 2 was mixed using a Silverson mixer (Model L22R, Silverson machines. Ltd, Waterside, England) operated at the lowest speed setting. After mixing for 5 minutes, 184.2 g of the homogenized organosol at 16.75% (w/w) solids

25   in NORPAR 12 solvent were combined with 106.6 g of NORPAR 12 solvent, 5.14 g of Monarch 120 carbon black (Cabot Corporation, Billerica, Mass.), and 4.03 g of 5.11% Zirconium HEX-CEM solution (OMG Chemical Company, Cleveland, Ohio) in a 16 ounce glass jar. This mixture was then milled in a 0.5 liter vertical bead mill (Model 6TSG-1/4, Aimex Co.,Ltd., Tokyo, Japan) charged with 390 g of 1.3mm

30   diameter Potters glass beads (Potters Industries, Inc., Parsippany, NJ). The mill was

operated at 2000 rpm for 1.5 hours without cooling water circulating through the cooling jacket of the milling chamber.

A portion of this 12% (w/w) solids toner concentrate was diluted to approximately 3% (w/w). This dilute toner sample exhibited the following properties as determined using the test methods described above:

> Number Mean Particle Size: 0.324 micron
> Bulk Conductivity: 272 picoMhos/cm
> Percent Free Phase Conductivity: 24%
> Dynamic Mobility: 0.0412 micron-cm/[Volt-second]

This working strength toner was tested on the plating apparatus described previously. The reflection optical density (ROD) was greater than 1.2 at plating voltages greater than 450 volts.

Comparative Example B

A liquid toner was prepared following the procedure of Example 3 except that 192.9 g of the homogenized organosol from Comparative Example A at 16.0% (w/w) solids in NORPAR 12 solvent were combined with 96.5 g of NORPAR 12 solvent, 5.14 g of Monarch 120 carbon black, and 3.34 g of 5.11% Zirconium HEX-CEM solution to form the organosol. A portion of the 12% (w/w) solids toner concentrate was diluted to approximately 3% (w/w). This dilute toner sample exhibited the following properties as determined using the test methods described above:

> Number Mean Particle Size: 0.241 micron
> Bulk Conductivity: 204 picoMhos/cm
> Percent Free Phase Conductivity: 5%
> Dynamic Mobility: 0.0412 micron-cm/[Volt-second]

This working strength toner was tested on the plating apparatus described previously. The reflection optical density (ROD) was greater than 1.3 at plating voltages greater than 450 volts.

Blocking Testing

Laser printed solid blocks (100% coverage, optical density = 1.3) of the toners from Example 3 and Comparative Example B were printed on ordinary uncoated A4 paper (Xerox 4200 copier paper) and tested according to ASTM test method D1146 in a humidity chamber at 48±1°C and 75% relative humidity for 24 hours.

5   At the end of this period, the ink images printed using the toner from Example 3 showed no adhesive blocking or image damage when the image and paper were separated. Slight cohesive failure was observed for this ink but no image damage was observed when the sheets were separated.

In contrast, the ink images printed using the toner from Comparative Example 10 B showed adhesive blocking (ink to paper blocking, as would be observed in a printed stack of single-sided images, i.e. front to back), but showed no image damage when the image and paper were separated. Cohesive failure was observed for the ink images (ink to ink blocking), as would be observed in a printed stack of duplexed sheets. In addition, image damage was observed when the sheets were separated.

15   A number of embodiments of the invention have been described. Nevertheless, it will be understood that various modifications may be made without departing from the spirit and scope of the invention. Accordingly, other embodiments are within the scope of the following claims.

WHAT IS CLAIMED IS:

1. An organosol dispersion comprising:

   (a) a carrier liquid having a Kauri-Butanol number less than 30; and

   (b) a graft copolymer comprising a (co)polymeric steric stabilizer covalently
bonded to a thermoplastic (co)polymeric core that is insoluble in said carrier liquid,
wherein said thermoplastic core comprises units derived from 3,3,5-
trimethylcyclohexyl methacrylate.

2. An organosol dispersion according to claim 1 wherein said dispersion further
comprises a colorant.

3. An organosol dispersion according to any of the preceding claims wherein said
core comprises 1-30% by weight of said 3,3,5-trimethylcyclohexyl methacrylate
units.

4. An organosol dispersion according to any of the preceding claims wherein said
core further comprises units selected from the group consisting of $C_1 - C_5$ acrylate
and methacrylate esters, styrene, and vinyl acetate.

5. An gel organosol dispersion according to any of the preceding claims wherein
said dispersion has a solids content of at least 2% by weight.

6. An organosol dispersion according to claim 1 wherein the ratio of said core to
said stabilizer on a weight to weight basis is between 1/1 and 15/1.

7. An organosol dispersion according to claim 2 wherein said colorant comprises
a pigment.

8. An organosol dispersion according to claim 7 wherein the ratio of said graft
copolymer to said pigment on a weight to weight basis is between 1/1 and 20/1.

9. An organosol dispersion according to any of the preceding claims wherein said
dispersion further comprises a charge director.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   C08F290/12   G03G9/13

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   C08F   G03G   C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98 13731 A (MINNESOTA MINING & MFG) 2 April 1998 (1998-04-02) the whole document	1-9
A	WO 97 12284 A (MINNESOTA MINING & MFG) 3 April 1997 (1997-04-03) the whole document	1-9
A	EP 0 851 013 A (DU PONT) 1 July 1998 (1998-07-01) page 4, line 7-12	1
A	US 3 991 226 A (KOSEL GEORGE E) 9 November 1976 (1976-11-09) cited in the application claims 1,6	1

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[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 September 2001	01/10/2001

Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 753 763 A (MIKELSONS VALDIS ET AL) 19 May 1998 (1998-05-19) claim 1	1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

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